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END OF THE YEAR REPORT

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DISSOLUTION INHIBITION IN POSITIVE NOVOLAK RESISTS

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PART I

a. Papers Submitted

T.F. Yeh, H.Y. Shih and A. Reiser,
"A Percolation View of Novolak Dissolution and Dissolution
Inhibition", submitted to Macromolecules.

T.F. Yeh, H.Y. Shih and A. Reiser,
"Dissolution Inhibition of Novolak in Bases",
submitted to Proc. SPIE, vol 1672.

A.A. Lin, H.Y. Shih and A. Reiser,
"Reactant Preordering in Solid Photopolymers",
submitted to Pure Applied Chem., Photochem. vol.13.

b. Papers Published

T.F. Yeh, H.Y. Shih, A. Reiser, M.A. Toukhy and B.T. Beauchemin
"Quantitative Description of Dissolution and Dissolution Inhibition
in Novolak and other Phenolic Resins"
J. Vac. Sci. Technol. B 10 (2) (1992).

h. Invited Presentations

A. Reiser: "Novolak Dissolution as a Percolation Process",
University of Canterbury, England, February 6, 1992.

A. Reiser: "The Mechanism of Dissolution Inhibition in Phenolic Resins",
Cornell University, May 4, 1992.

A. Reiser: "Positive Photoresists based on Dissolution Inhibition",
Ciba-Geigy, Fribourg, Switzerland, May 29, 1992.

Presentations

A.Reiser: "A Percolation View of Novolak Dissolution and Dissolution Inhibition",
SPIE Symposium on Microlithography, San Jose, March 9, 1992.

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PART 11

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d. Brief Description of Project

The inhibition of novolak dissolution by various light-sensitive compounds is the basis of the most important imaging materials of the semiconductor device industry. A formidable amount of empirical information on these systems is available in the literature, yet in spite of this the molecular mechanism of the inhibition phenomenon is not understood and progress in this area is made largely by trial and error.

The purpose of this part of the project is to develop a mechanistic model of dissolution and dissolution inhibition in the hope that this will serve as the basis of a more rational optimization of resist materials.

e. Significant Results this Year

The dimensionless description of the dissolution of phenolic resins described in last years report (also J. Vac. Sci. Techn. vol B 10 (2), 1992) has enabled us to consider a wide range of experimental data. It was realized from these results that the key to an understanding of the dissolution process is the recognition that novolak and other phenolic resins are amphiphilic materials. A novolak film may in effect be regarded as a hydrophobic body in which hydrophilic sites, (the OH groups of phenol), are embedded. Base diffuses into the solid matrix by a series of transfers or jumps from one hydrophilic site to the next. This view brings novolak dissolution into the realm of percolation theory.

Percolation theory describes diffusion as the progression of a mobile particle through a system of cells, some of which are "occupied", others empty. The particle is only allowed to reside in occupied cells,

and it may transfer from one occupied cell to its occupied neighbor, but it cannot reach a non-nearest neighbor directly. The movement of the particle is, therefore, restricted to a cluster of occupied cells in which it happens to be located. Fig.1 is a schematic representation of such a percolation field.

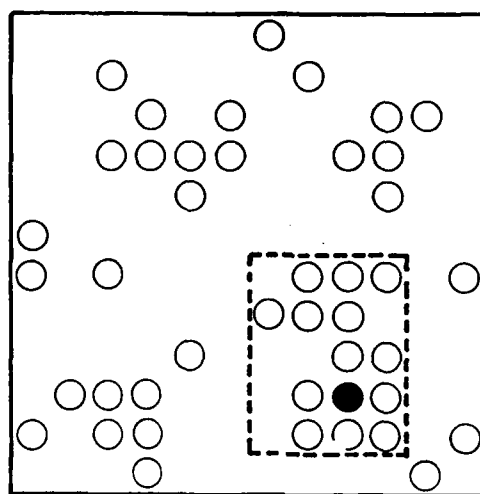


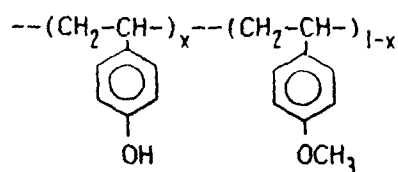
Figure 1 A two-dimensional percolation field. Only the occupied cells are indicated by open circles. The full circle is the diffusing molecule.

The state of the percolation field is characterized by the fraction, p , of occupied cells. As the number of occupied cells increases so does the average size of the cell clusters and so does the value of p . Continuous diffusion throughout the percolation field becomes possible when at least one "infinite" cluster has formed, i.e. a cluster which extends through the whole of the field. The p -value at which the first infinite cluster appears is called the percolation threshold, p_c .

In its stationary phase the dissolution process is controlled by the diffusion of base through a thin penetration zone which separates the matrix from the developer solution. As a result, novolak dissolution can be described by a scaling law derived for percolative diffusion in three dimensions:

$$R = \text{constant } (p - p_c)^2 \quad (1)$$

We have tested this scaling law on a series of partially methylated poly(vinylphenol) resins. Their general structure is shown below.



The result of this test is shown in Fig.2 where we have plotted $\log R$ against $\log(p - p_c)$ and obtained a straight line with a slope of 2, as required by theory.

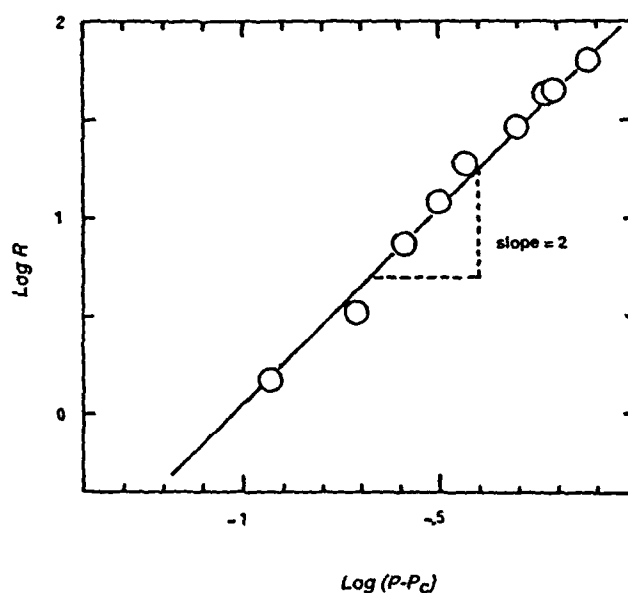


Figure 2 Test of the scaling law of equation 1.

An insight into the nature of inhibition is provided by a comparison of the dissolution of a resin to which increasing quantities of an inhibitor have been added, with the dissolution behavior of a series of partially methylated poly(vinylphenols). This is illustrated in Fig.3. The similarity between the two representations suggests that the addition of an inhibitor to a phenolic resin is tantamount to a reduction in the number of free phenol groups; both interventions correspond to a lowering of the percolation parameter p .

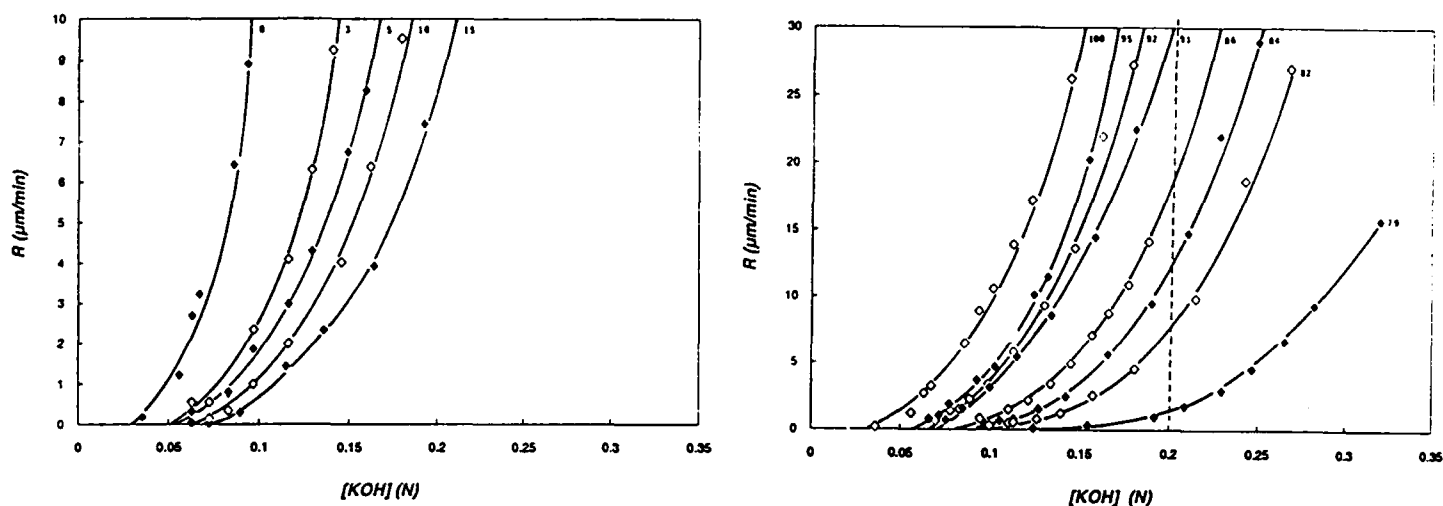


Figure 3 The dissolution rate as a function of base concentration (normality of KOH) in the developer. Left: poly(vinylphenol) in the presence of increasing quantities (weight %) of a diazoquinone inhibitor. Right: A series of partially methylated poly(vinylphenol) resins. The numbers on the curves indicate mol % of free phenol groups.

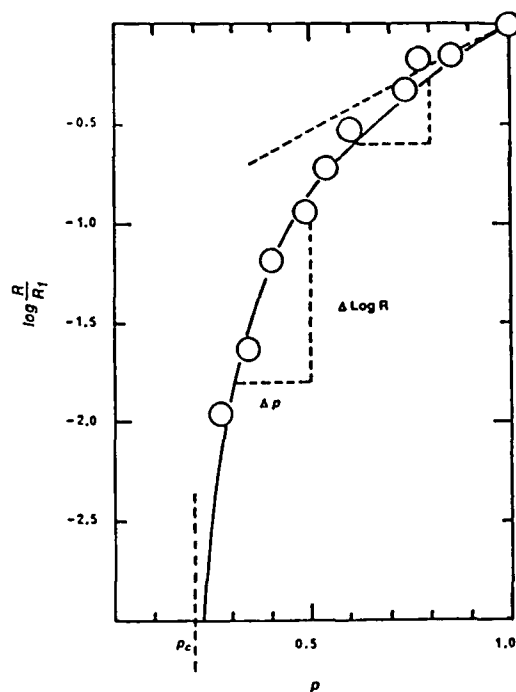


Figure 4. A plot of equation 1 in the form of $\log R$ as a function of p . The experimental point refer to the partially methylated poly(vinylphenols).

To visualize the implications of this statement, a plot of $\log R$ against p , derived from the percolative scaling law, eq 1, is shown in Fig.4. In this plot the addition of a certain amount of inhibitor translates the image point of the resin by a fixed horizontal distance towards lower values of p , and as a result, the dissolution rate of the doped resin (the resist) decreases. It can be seen that this inhibition effect is significantly more important in a slowly dissolving resin with an image point near the percolation threshold than it is in a fast dissolving resin near $p = 1$.

The link between inhibition and dissolution rate implied by the construction in Fig.4 was discovered empirically by resist designers a long time ago. Percolation theory provides now an intuitive understanding of the phenomenon and leads to a quantitative description by the equation shown below.

$$\frac{d \log R}{d c_i} = - f_{ij} = - \text{const.} \frac{d \log R}{d p} \quad (2)$$

Here, the first derivative is termed the inhibition factor, f_{ij} , of inhibitor i in resin j , and the derivative on the right hand side is the slope of the curve on Fig.4. This relationship has been tested on the group of partially methylated poly(vinylphenol) resins mentioned earlier by measuring the dissolution rate of the resins as well as the inhibition factor of a generic inhibitor in each one of them.

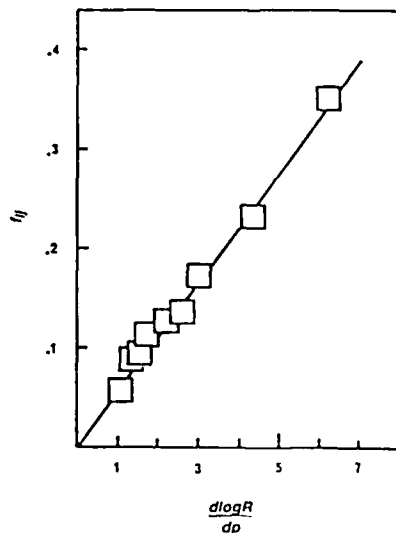


Figure 5. Test of equation 2 describing the relation between inhibition effect and the dissolution rate of the base resin.

The results are shown in Fig.5. The straight line obtained confirms the validity of eq 2; its slope is an absolute measure of the inhibition capability of the additive (inhibitor) without reference to any specific resin.

It is the merit of the percolation model that it promotes an intuitive grasp of the mechanism of dissolution and dissolution inhibition: all the qualitative and quantitative features of these systems flow from a single mental picture: the percolation field of the hydrophilic sites of the resin. The model points the way to the systematic optimization of resist materials. The image point of a resin to be used as resist should be chosen as near as possible to the percolation threshold in Fig.4. This will ensure a large inhibition effect and high photographic efficiency. Practical considerations, such as the necessity of a reasonable dissolution speed, will limit the attainment of the ultimate contrast, but the direction in which progress can be made is now clearly understood.

f. Summary of Plans for Next Year

1. Investigate the generality of the percolation model on a range of resins of different type, primary and tertiary structure. Examples: poly(4-hydroxystyrene) substituted in the 3-,2- and 5-position by sterically significant groups; poly(2-hydroxystyrene); meta/para-cresol based novolaks and ortho/para based novolaks. Most of these have now been introduced to the commercial resist market.

2. Develop methods by which the percolation characteristics of resins can be estimated from their molecular structure.

3. Investigate the interaction between the phenol groups of the resin (or more generally, the hydrophilic groups of the resin) and the anchor groups of the inhibitors. Investigate the effect of the size and spatial extension of the hydrophobic shield of the inhibitors on the dissolution rate of a standard resin. The results of this would provide a means of optimizing the structure of the inhibiting additive.

All these investigations have been started in a preliminary way, and all show promise.

g. Post Doctoral Fellow

Dr. Tung-Feng YEH